

cis-Trichlorotrakis(2,6-dimethyl-4-pyrone)gadolinium(III), [GdCl₃(C₇H₈O₂)₃]

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Abstract. $M_r = 635.67$, monoclinic, $P2_1/c$, $a = 10.612$ (8), $b = 14.759$ (7), $c = 18.028$ (9) Å, $\beta = 120.07$ (3)°, $V = 2444$ (3) Å³, $Z = 4$, $D_x = 1.73$ g cm⁻³, Mo K α , $\lambda = 0.71069$ Å, $\mu = 31.6$ cm⁻¹, $F(000) = 1252$, $T = 293$ K, final $R = 0.046$ for 5657 unique observed reflections. The discrete monomeric units each consist of a Gd^{III} ion coordinated by three 2,6-dimethyl-4-pyrone ligands *via* the carbonyl oxygen and by three Cl⁻; the slightly distorted octahedral coordination is not common in lanthanoids. Gd–O distances: 2.328 (6), 2.328 (5), 2.355 (5) Å; Gd–Cl distances: 2.622 (2), 2.634 (3), 2.645 (3) Å. The three 2,6-dimethyl-4-pyrone ligands have slightly longer C=O bonds than that found in the uncoordinated compound; other bond lengths and angles are normal.

Introduction. The coordination chemistry of yttrium and lanthanoids is dominated by large coordination numbers, figures less than seven being quite rare (Thompson, 1979). The synthesis and properties of a series of complexes [LnCl₃(dmp)₃] (dmp is 2,6-dimethyl-4-pyrone) have been described (Castellani Bisi, 1970); the low solubility of the compounds in suitable solvents and their thermodecomposition precluded molecular-weight determinations by colligative measurements or mass spectroscopy. By using the poorly coordinating perchlorate as anion, synthesis of complexes [Ln(dmp)_n](ClO₄)₃ was performed, with maximum $n = 8$ in the range La–Sm and $n = 7$ in the range Eu–Yb; however, complexes with $n = 6$ were also obtained in a deficiency of ligand, either for lighter or for heavier lanthanoids (La, Gd, Yb), thus supporting the possibility of six coordination. In order to establish the coordination number in trichloro complexes – where polymeric forms involving halogen bridges could allow figures higher than six – the crystal structure investigation of [GdCl₃(dmp)₃], chosen as typical of the series, has been undertaken.

Experimental. Colorless prismatic crystal 0.32 × 0.29 × 0.28 mm sealed in capillary under nitrogen to avoid moisture-induced decomposition. Philips PW1100 diffractometer; 25 reflections for lattice-

parameter measurements (θ range: 11.6–18.6°); refinement with LAT Philips routine using 9 reflections with $\theta \leq 30^\circ$; 7438 independent reflections with $\theta \leq 30^\circ$ [($\sin\theta/\lambda \leq 0.70$ Å⁻¹); $+h +k +l$ set, *i.e.* no equivalent reflections, max. $h = 13$, $k = 20$, $l = 25$; 1781 rejected as too weak [$I \leq 3\sigma(I)$]; no significant intensity deterioration of 3 standard reflections (220, 404, 055); Lp correction; absorption correction for sphere of equal volume (max. and min. corrections: 1.000 and 0.982); Patterson structure determination; full-matrix least-squares refinement on F by ORFLS (Busing, Martin & Levy, 1962); $w = 1$ for all reflections; anisotropic thermal parameters for all non-H atoms; occupancy refined for Gd against Gd³⁺ with final ratio 0.946:0.054; secondary-extinction coefficient according to Zachariasen (1963), refined to final $g = 2.2$ (2) × 10⁻⁵; atomic scattering factors with anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974); six H atoms, of pyrone CH groups, clearly detected on final ΔF Fourier map included in calculation, not refined; some methyl H's poorly detected and not introduced; final $R = 0.046$ ($R = 0.051$ including unobserved reflections with $|F| = 0.67|F_{\min, \text{obs}}|$ in their zone); $R_w = 0.056$ ($w = 1/\sigma_p^2$); $S = 1.24$; (Δ/σ)_{max} = 0.12; $\Delta\rho$ excursions between -0.54 and $+0.69$ e Å⁻³.*

Discussion. Table 1 shows the atomic parameters and Table 2 the bond distances and angles. The crystal structure, shown in Figs. 1 and 2, consists of monomeric units comprising a Gd^{III} ion coordinated to three dmp ligands through the carbonyl oxygen atoms and to three chloride ions. The coordination polyhedron is an octahedron, where ligands of the same chemical type are in the *cis* configuration. The octahedron is slightly distorted, as the two groups of Gd–O and Gd–Cl distances are quite different (*i.e.* one of the bases of the

* Lists of structure factors, anisotropic thermal parameters, unrefined H-atom parameters and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39533 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

trigonal antiprism is nearer to Gd than the other). A comparison can be made between these distances and those found in the only other known complex of similar structure: trichlorotriss(hexamethylphosphoramide)praseodymium(III) (Radonovich & Glick, 1973), which is also octahedral, with three metal-oxygen and three metal-chlorine bonds. The average Pr-O bond length is 2.35 and Pr-Cl 2.72 Å. The difference between the average Gd-Cl and Pr-Cl bond lengths (0.08 Å) is in a very good agreement with the difference in the ionic radii of the two cations [0.075 Å using values from Shannon & Prewitt (1969)].

Table 1. Atomic coordinates ($\times 10^4$; $\times 10^5$ for Gd) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

B_{eq} is calculated according to Hamilton (1959).

| | x | y | z | $B_{eq}(\text{Å}^2)$ |
|-------|-----------|-----------|-----------|----------------------|
| Gd | 22257 (4) | 20255 (2) | 23833 (2) | 2.36 (1) |
| Cl(1) | 894 (3) | 468 (2) | 1819 (2) | 4.7 (1) |
| Cl(2) | 4679 (3) | 1485 (2) | 2479 (2) | 4.0 (1) |
| Cl(3) | 1139 (3) | 2850 (2) | 891 (2) | 3.5 (1) |
| O(1) | 3062 (7) | 1566 (4) | 3790 (4) | 3.7 (1) |
| C(1) | 4088 (9) | 1388 (5) | 4534 (5) | 2.9 (1) |
| C(2) | 5542 (9) | 1219 (6) | 4717 (5) | 3.3 (3) |
| C(3) | 3852 (8) | 1360 (5) | 5251 (5) | 2.9 (2) |
| C(4) | 6604 (9) | 1042 (6) | 5527 (6) | 3.3 (3) |
| C(5) | 4965 (8) | 1172 (5) | 6042 (5) | 2.9 (3) |
| O(2) | 6326 (6) | 1010 (4) | 6175 (4) | 3.4 (2) |
| C(6) | 8169 (9) | 834 (8) | 5825 (7) | 5.3 (4) |
| C(7) | 4911 (9) | 1119 (7) | 6852 (5) | 3.9 (3) |
| O(3) | 3290 (7) | 3412 (4) | 3051 (4) | 3.8 (2) |
| C(8) | 3177 (8) | 3992 (5) | 3529 (5) | 3.0 (2) |
| C(9) | 3582 (9) | 4920 (5) | 3523 (5) | 3.2 (3) |
| C(10) | 2678 (8) | 3783 (5) | 4098 (5) | 3.0 (3) |
| C(11) | 3403 (8) | 5532 (5) | 4003 (5) | 3.1 (3) |
| C(12) | 2542 (8) | 4436 (5) | 4584 (5) | 3.0 (3) |
| O(4) | 2908 (6) | 5311 (4) | 4537 (3) | 3.2 (2) |
| C(13) | 3679 (9) | 6541 (5) | 4019 (6) | 4.5 (4) |
| C(14) | 1988 (9) | 4312 (6) | 5196 (6) | 4.5 (4) |
| O(5) | 302 (6) | 2519 (4) | 2554 (4) | 3.2 (2) |
| C(15) | -352 (7) | 2306 (5) | 2942 (5) | 2.7 (2) |
| C(16) | -564 (8) | 1383 (5) | 3115 (5) | 3.1 (3) |
| C(17) | -951 (8) | 2961 (5) | 3265 (5) | 3.2 (3) |
| C(18) | -1238 (8) | 1186 (5) | 3550 (5) | 3.0 (3) |
| C(19) | -1584 (8) | 2730 (5) | 3712 (5) | 3.2 (3) |
| O(6) | -1730 (5) | 1837 (4) | 3866 (3) | 3.1 (2) |
| C(20) | -2194 (8) | 3333 (5) | 4117 (5) | 4.7 (4) |
| C(21) | -1560 (9) | 254 (6) | 3755 (6) | 4.3 (4) |

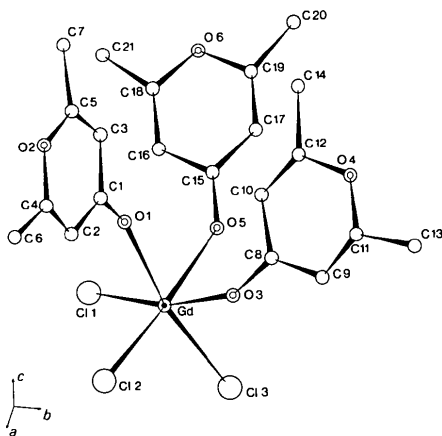


Fig. 1. Perspective view of the structure.

Table 2. Bond distances (Å) and angles ($^\circ$) and selected torsion angles ($^\circ$) with e.s.d.'s in parentheses

| | | | |
|----------------|-----------|---------------------|------------|
| Gd-Cl(1) | 2.622 (2) | Gd-O(1) | 2.328 (6) |
| Gd-Cl(2) | 2.645 (3) | Gd-O(3) | 2.355 (5) |
| Gd-Cl(3) | 2.634 (3) | Gd-O(5) | 2.328 (5) |
| Cl(1)-Gd-Cl(2) | 94.7 (1) | Cl(2)-Gd-O(5) | 170.2 (2) |
| Cl(1)-Gd-Cl(3) | 97.7 (1) | Cl(3)-Gd-O(1) | 168.4 (2) |
| Cl(1)-Gd-O(1) | 90.2 (2) | Cl(3)-Gd-O(3) | 88.5 (2) |
| Cl(1)-Gd-O(3) | 170.7 (2) | Cl(3)-Gd-O(5) | 91.5 (2) |
| Cl(1)-Gd-O(5) | 89.3 (2) | O(1)-Gd-O(3) | 82.7 (2) |
| Cl(2)-Gd-Cl(3) | 96.8 (1) | O(1)-Gd-O(5) | 80.1 (2) |
| Cl(2)-Gd-O(1) | 90.9 (2) | O(3)-Gd-O(5) | 83.6 (2) |
| Cl(2)-Gd-O(3) | 91.4 (2) | | |
| Gd-O(1)-C(1) | 151.0 (5) | Gd-O(1)-C(1)-C(2) | -17.6 (7) |
| Gd-O(3)-C(8) | 138.9 (5) | Gd-O(3)-C(8)-C(9) | -153.9 (6) |
| Gd-O(5)-C(15) | 140.0 (5) | Gd-O(5)-C(15)-C(16) | -33.6 (7) |
| O(1)-C(1) | 1.261 (9) | O(1)-C(1)-C(3) | 121.2 (7) |
| C(1)-C(2) | 1.43 (1) | O(1)-C(1)-C(2) | 122.6 (7) |
| C(2)-C(4) | 1.35 (1) | C(2)-C(1)-C(3) | 116.3 (7) |
| O(2)-C(4) | 1.342 (9) | C(1)-C(2)-C(4) | 120.2 (7) |
| C(4)-C(6) | 1.50 (1) | C(2)-C(4)-O(2) | 121.4 (7) |
| O(2)-C(5) | 1.361 (9) | C(2)-C(4)-C(6) | 127.0 (8) |
| C(3)-C(5) | 1.35 (1) | O(2)-C(4)-C(6) | 111.6 (7) |
| C(5)-C(7) | 1.49 (1) | C(4)-O(2)-C(5) | 121.1 (6) |
| C(1)-C(3) | 1.44 (1) | O(2)-C(5)-C(3) | 120.9 (7) |
| | | O(2)-C(5)-C(7) | 112.0 (7) |
| | | C(3)-C(5)-C(7) | 127.1 (7) |
| | | C(1)-C(3)-C(5) | 120.2 (7) |
| O(3)-C(8) | 1.262 (8) | O(3)-C(8)-C(10) | 123.3 (7) |
| C(8)-C(10) | 1.40 (1) | O(3)-C(8)-C(9) | 120.7 (7) |
| C(10)-C(12) | 1.36 (1) | C(9)-C(8)-C(10) | 116.0 (7) |
| O(4)-C(12) | 1.364 (9) | C(8)-C(10)-C(12) | 121.1 (7) |
| C(12)-C(14) | 1.50 (1) | C(10)-C(12)-O(4) | 120.4 (7) |
| O(4)-C(11) | 1.346 (9) | C(10)-C(12)-C(14) | 126.6 (7) |
| C(9)-C(11) | 1.33 (1) | O(4)-C(12)-C(14) | 113.0 (7) |
| C(11)-C(13) | 1.52 (1) | C(11)-O(4)-C(12) | 120.0 (6) |
| C(8)-C(9) | 1.44 (1) | O(4)-C(11)-C(9) | 122.4 (7) |
| | | O(4)-C(11)-C(13) | 111.4 (7) |
| | | C(9)-C(11)-C(13) | 126.2 (8) |
| | | C(8)-C(9)-C(11) | 120.2 (7) |
| O(5)-C(15) | 1.247 (9) | O(5)-C(15)-C(16) | 123.4 (7) |
| C(15)-C(16) | 1.44 (1) | O(5)-C(15)-C(17) | 122.9 (7) |
| C(16)-C(18) | 1.33 (1) | C(16)-C(15)-C(17) | 113.7 (7) |
| O(6)-C(18) | 1.350 (9) | C(15)-C(16)-C(18) | 121.5 (7) |
| C(18)-C(21) | 1.51 (1) | C(16)-C(18)-O(6) | 121.9 (7) |
| O(6)-C(19) | 1.372 (9) | C(16)-C(18)-C(21) | 126.8 (8) |
| C(17)-C(19) | 1.33 (1) | O(6)-C(18)-C(21) | 111.3 (7) |
| C(19)-C(20) | 1.489 (8) | C(18)-O(6)-C(19) | 119.5 (6) |
| C(15)-C(17) | 1.43 (1) | O(6)-C(19)-C(17) | 120.9 (7) |
| | | O(6)-C(19)-C(20) | 110.6 (6) |
| | | C(17)-C(19)-C(20) | 128.5 (7) |
| | | C(15)-C(17)-C(19) | 122.5 (7) |

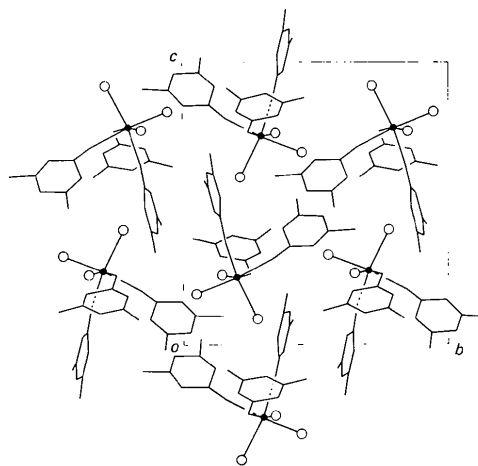


Fig. 2. Molecular packing viewed along a.

The three molecules of dmp, as far as bond distances and bond angles are concerned, are essentially equivalent; the carbonyl bond length is a little longer than that found in the uncoordinated ligand (Brown, Norment & Levy, 1957); this result is consistent with the shift to lower frequencies of the carbonyl stretching mode found in the IR spectrum of $[\text{GdCl}_3(\text{dmp})_3]$ relative to dmp. The other bond lengths and angles are in very good agreement with those found in the uncoordinated ligand and in the complex $[\text{Er}(\text{dmp})_7](\text{ClO}_4)_3$ (Castellani Bisi, Coda & Tazzoli, 1981). In $[\text{Gd}(\text{dmp})_7](\text{ClO}_4)_3$, gadolinium is coordinated by seven molecules of dmp. The larger size of the chloride ion compared to oxygen is consistent with the lower coordination number, six, in the title compound.

The minimum intermolecular distance (excluding H's) is $\text{Cl}(2)-\text{O}(6^i) = 3.39(1) \text{ \AA}$ [$i = 1+x, y, z$].

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catena-Aqua-di- μ -chloro-chloro(2,6-dimethyl-4-pyrone)lanthanum(III), $[\text{LaCl}_3(\text{C}_7\text{H}_8\text{O}_2)(\text{H}_2\text{O})]_n$

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Abstract. $M_r = 387.42$, monoclinic, $P2_1/m$, $a = 7.255(5)$, $b = 9.152(5)$, $c = 9.781(6) \text{ \AA}$, $\beta = 103.82(3)^\circ$, $V = 630.6(7) \text{ \AA}^3$, $Z = 2$, $D_x = 2.040 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 40.6 \text{ cm}^{-1}$, $F(000) = 368$, $T = 293 \text{ K}$, final $R = 7.9\%$ for 1734 unique observed reflections. Each La^{III} is coordinated by four equivalent Cl and a water O, which form the equatorial corners of a pentagonal bipyramid; the axial positions are occupied by a terminal Cl and the $\text{C}_7\text{H}_8\text{O}_2$ carbonyl O. The coordination polyhedra form polymeric chains by sharing equatorial edges of Cl atoms. $\text{La}-\text{O}(\text{C}_7\text{H}_8\text{O}_2) 2.33(2)$; $\text{La}-\text{O}(\text{H}_2\text{O}) 2.50(2)$; $\text{La}-\text{Cl}(\text{eq.}) 2.90, 2.92(1)$; $\text{La}-\text{Cl}(\text{ax.}) 2.72(1) \text{ \AA}$.

Introduction. As part of a study on the coordination number of lanthanoids and its variations with decreasing ionic radius of the cation, some years ago the series of complexes $[\text{LnCl}_3(\text{dmp})_3]$ (dmp = 2,6-dimethyl-4-pyrone; Ln = all lanthanoids except Pm) (Castellani Bisi, 1970) was prepared. The crystal structure of

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$[\text{GdCl}_3(\text{dmp})_3]$, typical of the series, was determined and the metal ion was found to have octahedral coordination geometry (Bisi Castellani & Tazzoli, 1984).

By operating with a deficiency of the ligand, for La only, the complex $[\text{LaCl}_3(\text{dmp})_2]$ was also obtained for which a polymeric structure involving Cl bridges was supposed, since a monomeric form would imply five coordination which is exceedingly rare for lanthanoids. Its crystal structure determination was not possible, since it has been invariably isolated as a powder. However, during repeated preparations a novel complex with formula $[\text{LaCl}_3(\text{dmp})(\text{H}_2\text{O})]$ was obtained, probably due to imperfect drying of the ethanol.

Experimental. A few crystals of the title compound were grown after mixing equimolar saturated ethanolic solutions of dmp and LaCl_3 without excluding atmospheric moisture and slowly evaporating the solvent at room temperature. Unfortunately, several subsequent trials no longer yielded the crystals; thus, at the

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